

APPENDIX C
COPPER RECYCLING

Contents

	<u>page</u>
C.1 Inventory of Potentially Recyclable Copper Scrap	C-1
C.1.1 Scrap Metal Inventory	C-1
C.1.2 Radionuclide Inventory	C-4
C.2 Recycling of Copper Scrap	C-6
C.2.1 Types of Copper Scrap	C-6
C.2.2 Scrap Handling and Preparation	C-8
C.2.3 Copper Refining Operations	C-10
C.2.3.1 Copper Smelting Practices	C-11
C.2.3.2 Copper Converting	C-18
C.2.3.3 Fire Refining	C-19
C.2.3.4 Electrolytic Refining	C-19
C.2.3.5 Melting, Casting, and Use of Cathodes	C-23
C.2.3.6 Slag Handling	C-23
C.2.3.7 Offgas Handling	C-24
C.2.3.8 Illustrative Secondary Smelter	C-24
C.2.4 Brass and Bronze Ingot Production	C-27
C.2.5 Brass Mills	C-27
C.2.6 Aluminum Bronze Foundries	C-30
C.3 Markets	C-31
C.3.1 Scrap Prices	C-31
C.3.2 Scrap Consumption	C-32
C.4 Partitioning of Contaminants	C-32
C.4.1 Partitioning During Copper Refining	C-33
C.4.1.1 Thermochemical Considerations	C-33
C.4.1.2 Experimental Partitioning Studies	C-33
C.4.1.3 Proposed Partitioning of Contaminants	C-38
C.4.2 Partitioning During Brass Smelting	C-46
C.5 Exposure Scenarios	C-46
C.5.1 Modeling Parameters	C-46
C.5.1.1 Dilution of Cleared Scrap	C-47
C.5.1.2 Slag Production	C-47
C.5.1.3 Baghouse Dusts	C-48
C.5.1.4 Electrolyte Bleed	C-49
C.5.1.5 Anode Slimes	C-49
C.5.1.6 Summary Model for Fire-Refined Products	C-50
C.5.1.7 Summary Model for Electrorefining	C-51

Contents (continued)

	<u>page</u>
C.5.2 Worker Exposures	C-51
C.5.2.1 Baghouse Dust Agglomeration Operator	C-52
C.5.2.2 Furnace Operator	C-53
C.5.2.3 Scrap Handler	C-53
C.5.2.4 Casting Machine Operator	C-53
C.5.2.5 Scrap Metal Transporter	C-53
C.5.2.6 Tank House Operator	C-54
C.5.3 Non-Industrial Exposures	C-54
C.5.3.1 Driver of Motor Vehicle	C-54
C.5.3.2 Homemaker	C-54
References	C-56
Appendix C-1. Partitioning During Fire Refining and Electrorefining of Copper Scrap	

Tables

	<u>page</u>
C-1. Current Inventory of Copper Scrap at DOE Facilities	C-2
C-2. Availability of Copper from Decommissioning of Nuclear Facilities	C-5
C-3. Copper Recovered from Scrap Metal Processed in the United States in 1997	C-10
C-4. Copper Consumption from Copper-Base Scrap in the United States in 1997	C-11
C-5. Composition of Process Streams from the Smelting of Copper Scrap in a Cupola Blast Furnace	C-13
C-6. Composition of Products Obtained from Treating Copper Blast Furnace Slag in an EAF	C-15
C-7. Partitioning During Blast Furnace Smelting of Copper Scrap	C-15
C-8. Composition of Converter Products from the Smelting of Copper Scrap	C-19
C-9. Composition of Anodes Produced in a 250-t Reverberatory Furnace	C-20
C-10. Anode Compositions at Various U.S. Electrolytic Copper Refineries	C-22
C-11. Consumption of Copper-Base Scrap in 1997	C-29
C-12. Standard Free Energies of Formation for Various Oxides at 1,500 K	C-35
C-13. Calculated Partition Ratios of Various Contaminants Between Copper and an Oxide Slag at 1,400 K	C-36
C-14. Partitioning of Uranium in Laboratory Melts of Copper	C-37
C-15. Distribution of Iridium and Ruthenium During Electrorefining of Copper	C-37
C-16. Distribution of Iridium and Ruthenium after Electrolyte Purification	C-38
C-17. Observed Partition Fractions in the Melting of Low-grade Copper in a Blast Furnace	C-39
C-18. Partition Fractions of Impurities in the Melting of Low-grade Copper Scrap in a Blast Furnace	C-40
C-19. Partition Fractions of Impurities in the Fire Refining of Copper	C-42
C-20. Composition of Anode and Cathode Copper and Anode Slimes at the Southwire Co.	C-43
C-21. Partition Fractions of Impurities in the Electrorefining of Copper	C-44
C-22. Half-cell Electrode Potentials of Elements less Noble than Copper	C-45
C-23. Airborne Dust Concentrations At Primary Copper Smelter	C-52
 C1-1. Partitioning During Fire Refining and Electrolysis of Copper Scrap	 C1-1

Figures

C-1. Simplified flow diagram for copper-base scrap in 1997	C-9
C-2. Process diagram for the flow of copper scrap in primary and secondary copper refining.	C-12
C-3. Flow Diagram of the Copper Division of Southwire (CDS)	C-26
C-4. Proposed Material Balance for Modeling Copper Produced by Fire Refining	C-51
C-5. Simplified Material Balance for Electrorefining of Copper Produced from Scrap	C-52

COPPER RECYCLING

This appendix presents background material to support an analysis of exposures expected from the recycling of copper scrap.

C.1 INVENTORY OF POTENTIALLY RECYCLABLE COPPER SCRAP

C.1.1 Scrap Metal Inventory

The Scrap Metal and Equipment Appendix to the 1996 MIN Report (U.S. DOE 1995) identified 1,691 metric tons¹ (t) of copper and brass scrap in inventory. This inventory was classified as containing 1,490 t of contaminated metal, 53 t of clean scrap metal, and 148 t of material unspecified as to its state of contamination. (These amounts are slightly higher than the inventory listed in Table 4-4 of the present report)². A detailed breakdown by location is provided in Table C-1. Based on the ratio of clean to contaminated scrap, 143 t of the unspecified material was categorized in the present study as contaminated, resulting in a total of 1,633 t of potentially contaminated 58 t of clean copper and brass scrap. As discussed in Section 4.1.4, the HAZWRAP Report (Parsons 1995) listed inventories of contaminated scrap metal at LANL and Rocky Flats which were omitted from the MIN Report. It is therefore likely that some unreported copper scrap may be in inventory at these two sites.

Obviously, most of the current inventory is at Fernald. DOE has entered into an arrangement with Decon and Recovery Services LLC (DRS) of Oak Ridge, Tenn. to process about 1,200 t of copper scrap (primarily motor windings) from Fernald (Deacon 1999). DRS will mechanically remove the insulation, which is slightly contaminated, leaving behind clean copper that, in the future, could be released for unrestricted sale under the provisions of DOE Order 5400.5.³

¹ This appendix includes numerous references with widely varying units of measurement. The authors of this appendix have generally chosen not to convert the units to a consistent system but rather have chosen to quote information from the various sources in the original units. When the cited information is distilled into scenarios for modeling doses and risks, consistent units are used.

² These data are slightly higher than those in Summary Table 1.4 of U.S. DOE 1995 because that table did not include all individual sites.

³ As noted in Chapter 2, DOE currently has a moratorium on the free release of volumetrically contaminated metals and has suspended the unrestricted release for recycling of scrap metal from radiological areas within DOE facilities.

Table C-1. Current Inventory of Copper Scrap at DOE Facilities (t)

Location	Clean	Contaminated	Unspecified
Fernald		1270	
ANL-W	6.3		
Hanford	33		
BNL		200	
FermiLab		9.2	
SRS	2.5	11	
WIPP	0.23		
NTS	0.90		
SLAC	4.8		
LBL	4.8		
K-25			42
Y-12			44
ORNL			1.8
Portsmouth			21
Paducah			39
Total	53	1490	148

The principal future sources of DOE copper scrap are the gaseous diffusion plants at Oak Ridge; Paducah, Ky., and Portsmouth, Ohio. It has been estimated that these plants contain 40,200 t of copper scrap (National Research Council 1996)⁴ with individual facility totals as follows:

- K-25 16,000 t
- Portsmouth 13,600 t
- Paducah 10,600 t

The copper is present in the form of wire, tubing, and valves, with the following breakdown reported for the K-25 plant (U.S. DOE 1993):

⁴ These values were derived from a 1991 study by Ebasco Services, Inc., which estimated that the total radioactive scrap metal arising from decommissioning the three gaseous diffusion plants would be 642,000 t. This estimate did not include carbon steel in the building structures but did include electrical/instrumentation equipment and housings. Person et al. (1995) estimated that 1,047,000 t of scrap metal would be recycled including structural steel. Of this total, 60.3% is estimated to be potentially contaminated and the balance to be clean. Thus, these authors predicted the same total amount of radioactive scrap metal as the earlier Ebasco study; they did not provide a breakdown by metal type.

- copper tubing/valves 0.19 t
- large copper wire 8.6 t
- small copper wire 7.2 t

The three plants contain an additional 20,200 t of "aluminum/copper," but the two metals are not separated by type. The above estimates do not include any copper in "miscellaneous electrical/instrumentation and housings" (U.S. DOE 1993). No information is available on copper scrap expected to be generated at other DOE facilities.

To develop a recycling schedule for DOE facilities, the procedure described below was used. Existing scrap is assumed to be available for processing in 2003. The existing inventory is adjusted to remove the Fernald motor windings, since this scrap is being handled currently. The decommissioning schedule for the three diffusion plants is as follows (see Section 4.1.5):

- K-25 1998-2006
- Portsmouth 2007-2015
- Paducah 2015-2023

It is assumed that no scrap is generated in the first year of a nine-year decommissioning period, 13% is generated in years 2 through 8, and 9% in the final year. Scrap generation based on this schedule is summarized in Table C-2.

Table A-29 lists the amounts of copper, brass, and bronze used to construct a 1971-vintage, 1,000 MWe PWR facility. Specific information is not available on the amount or contamination level of radioactively contaminated copper scrap that would be generated during the decommissioning of such a facility. Consequently, it is assumed that the contaminated fraction of copper scrap is the same as contaminated fraction of carbon steel from the Reference BWR and Reference PWR facilities.

Extending the data in Table A-29 to the entire U.S. commercial nuclear power industry leads to the conclusion that approximately 73,000 t of copper would be generated by the decommissioning of the facilities listed in Appendix A-1. Only a small portion of this metal is expected to be contaminated. Some of the contaminated inventory may not be suitable for free release. Based on the results for carbon steel presented in Appendix A, it is assumed that 20% of the copper scrap from the Reference BWR would be residually radioactive metal that is potentially

recyclable, while 10% of the copper scrap from the Reference PWR would fall into this category. Applying these factors yields 9,691 t of potentially recyclable contaminated copper, as shown in Table 4-8. As shown in that table, the nuclear power plants also contain small quantities of brass and bronze. These copper alloys were not included in this analysis. Since the annual availability of these alloys should be less than 50 t in toto, sizable dilution with uncontaminated scrap is expected; thus, the omission of these metals should have no significant impact on the radiological assessment.

The schedule of anticipated releases of scrap metals from nuclear power plants is presented in Table 4-9. The data for copper are reproduced in Table C-2.

From Table C-2, it can be seen that the maximum projected annual amount of DOE and commercial nuclear power plant copper scrap to be available for clearance is 10,833 t in the year 2003. This includes the 1,633-t inventory derived from U.S. DOE 1995 (less 1,200 t of Fernald scrap assumed to have been removed to date), and a stockpile of copper scrap accumulated during five years (1999 - 2003) of decommissioning and dismantlement of the K-25 facility. This projection is based on the assumption that DOE will resume clearing scrap metal for recycle by 2003 (see Section B.1.1). The total of 50,300 t of potentially recyclable scrap in Table C-2 is in good agreement with a more recent DOE estimate of 51,000 t of radioactive copper scrap (Adams 1998).

C.1.2 Radionuclide Inventory

As indicated in Section C.1.1, the majority of scrap copper will be generated from the gaseous diffusion plants. The naturally occurring uranium isotopes and their short-lived progenies are the principal source of contamination at the diffusion plants. Other contaminants include Tc-99, U-236, and traces of Pu-239 and Np-237. It has been estimated that the following activities were introduced into the Paducah gaseous diffusion plant, relative to 250 kCi of U-238 (National Research Council 1996):

• U-236	900 Ci
• Tc-99	11,200 Ci
• Np-237	13 Ci
• Pu-239	20 Ci
• Th-230 (+ progeny)	140 Ci

• Pa-231 (+ progeny) 16 Ci

Table C-2. Availability of Copper from Decommissioning of Nuclear Facilities (t)

Year	DOE Facilities	Commercial Nuclear Power Plants	Year	Commercial Nuclear Power Plants
2003	10,833	—	2027	207
2004	2,080	—	2028	247
2005	2,080	—	2030	215
2006	1,440	103	2031	285
2007	—	24	2032	673
2008	1,770	—	2033	425
2009	1,770	—	2034	711
2010	1,770	—	2035	564
2011	1,770	—	2036	954
2012	1,770	—	2037	374
2013	1,770	—	2038	129
2014	1,770	—	2039	286
2015	1,210	—	2040	77
2016	1,380	115	2043	201
2017	1,380	—	2044	124
2018	1,380	—	2045	75
2019	1,380	235	2046	62
2020	1,380	189	2047	19
2021	1,380	172	2049	62
2022	1,380	537	2052	38
2023	940	654	2056	69
2024	—	1,074	2057	69
2025	—	132	2058	98
2026	—	517		
Total	40,633			9,715

Much of this contamination was removed during the cascade upgrade and improvement programs of the 1980's (National Research Council 1996). The other significant source of copper scrap is Fernald. Beginning in 1953, the Feed Materials Production Center (now known as the Fernald Environmental Management Project [FEMP]) converted uranium ore to uranium metal

targets for nuclear weapons production. Over a 36-year period, this facility produced over 225,000 t of purified uranium. The principal radioactive contaminants include the uranium isotopes (and their short-lived progenies) and Tc-99.

In commercial nuclear power plants, activation of copper should be negligible. Naturally occurring copper consists of two isotopes: Cu-63 (69%) and Cu-65 (31%). In a nuclear power reactor, thermal neutrons create only small amounts of Cu-64 and Cu-66, because the neutron-capture cross-sections of the naturally-occurring copper isotopes are small. These radioisotopes, with respective half-lives of 12.7 hr and 5.1 min, undergo β -decay to the stable isotopes Zn-64 and Zn-66. Thus, the major source of radioactive contamination will be surface contamination caused by a broad suite of radionuclides (Epel 1997).

C.2 RECYCLING OF COPPER SCRAP

Copper scrap can enter copper refining and processing operations in a variety of ways, depending on factors such as the quality of the scrap and its alloy content. For example, some copper scrap may be refined at primary copper smelters and some at secondary smelters. Copper alloy scrap may be remelted at brass mills, ingot makers, or foundries. This section characterizes the manner in which copper and copper alloy scrap are recycled.

C.2.1 Types of Copper Scrap

The Institute of Scrap Recycling Industries (ISRI) and the National Association of Recycling Industries recognize various major classes of copper scrap (NARI 1980, Newell 1982, Riley et al. 1984). The major unalloyed scrap categories are termed No. 1 copper, which must contain more than 99% copper, and No. 2 copper, which must contain a minimum of 94% copper. For copper alloys, ISRI has identified 50 separate scrap classifications. Additional classifications exist for copper containing waste streams, such as skimmings, ashes and residues generated in copper smelting and refining processes.

Copper scrap is further categorized as either “old” or “new” scrap. New scrap is generated during fabrication of copper products. For example, copper-containing end-products that are manufactured from intermediates, such as copper sheet, strip, piping, or rod, may have product yields as low as 40%. These new scrap materials generated from borings, turnings, stampings, cuttings, and “off-specification” products are commonly sold back to the mills that produced the original intermediates from which the new scrap was generated. Since both new scrap and

manufactured scrap are recycled within the copper industry, neither is considered to be a new source of copper.

Old scrap, which is generated from worn-out, discarded, or obsolete copper products, does constitute a new (i.e., from outside the industry) source of metal for the secondary copper industry. Since World War II, the reservoir of copper products in use has increased dramatically, both in the U.S. and globally. The U.S. scrap inventory increased from 16.2 million tons in 1940 to nearly 70 million tons in 1991 (Bureau of Mines 1993). The availability of copper scrap is linked with the quantity of copper-containing products and their life-cycles. Estimates of life cycles have been made for major products: copper used in electrical plants and machinery averages about 30 years, in non-electrical machinery about 15 years, in housing 40 years or more, and in transportation about 10 years (Carlin et al. 1995).

Copper scrap may also be broadly categorized into four main types based on copper content and the manner in which it is treated for copper recovery (as quoted from Davenport 1986):

- Low-grade scrap of variable composition (10-95% Cu). This material is smelted in blast or hearth furnaces and then fire and electrolytically refined. It may also be treated in Peirce-Smith converters of primary smelters.
- Alloy scrap, the largest component of the scrap recovery system, consists mainly of brasses, bronzes, and cupronickels from new and old scrap. There is no advantage in re-refining these alloys to pure copper, and hence they are remelted in rotary, hearth, or induction furnaces and recast as alloy stock. Some refining is done by air oxidation to remove aluminum, silicon, and iron as slag, but the amount of oxidation must be closely controlled because desirable alloy constituents (Zn in brasses and Sn in bronzes) also tend to oxidize.
- Scrap, new or old, which is by and large pure copper but which is contaminated by other metals (e.g. metals used in plating, welding, or joining). This scrap, is melted in the Peirce-Smith converters of primary smelters or the anode furnaces of primary or secondary refineries, where large portions of the impurities (e.g. Al, Fe, Zn, Si, Sn) are removed by air oxidation. The metal is then cast into copper anodes and electro-refined It may also be sold as fire-refined copper for alloy making.
- Scrap which is of cathode quality and requires only melting and casting. This scrap originates mainly as wastes from manufacturing (e.g. reject rod, bare wire, molds). It is melted and cast as ingot copper or alloyed and cast as brasses or bronzes.

According to the U.S. Geological Survey, in 1997, about 496,000 t of copper were recovered from old scrap and 956,000 t from new scrap. This resulted in 1,450,000 t of copper consumption in the U.S. from scrap (Edelstein 1998). This quantity of copper was contained in 1,750,000 t of scrap metal. Table C-3 summarizes the kinds of scrap involved in copper recycle and the form in which the copper was recovered. It is important to note that alloy scrap will typically be reused in similar alloys. Aluminum scrap containing copper will be used in aluminum alloys; brass scrap will be used in brass, etc. However, pure recycled copper can conceptually be used either as pure copper or as an alloying agent.

In 1997, consumers of this scrap included about 35 brass mills, several brass and bronze ingot makers, 15 wire mills, four secondary smelters, seven primary smelters, six fire refineries, eight electrolytic plants, and 600 foundries, chemical plants, and miscellaneous consumers (USGS 1998). The quantities of old and new copper-base scrap used by these consumers are summarized in Table C-4. The total in this table is less than the total in Table C-3 because Table C-4 includes only copper-base but not other copper-containing scrap.

A simplified flow diagram for the copper scrap consumption documented in Table C-4 is included as Figure C-1. This figure illustrates the disposition of 1,370,000 t of copper in copper-base scrap. It is apparent from the diagram that the flow paths are numerous and complex. Information presented by Edelstein (1998) indicates that, of the 383,000 t of copper in scrap that is processed by smelters and refiners (i.e. the box on the left of Figure C-1), about 39% is No. 1 wire and heavy scrap. Although Figure C-1 indicates that scrap was processed by four secondary smelters in 1997, currently only two secondary smelters are operating (Chemetco in Hartford, Ill. and Southwire in Carrollton, Ga). Chemetco produces anodes, which are sent to another processor (Asarco) for electrolytic refining. Southwire does its own electrolytic refining.

C.2.2 Scrap Handling and Preparation

Copper scrap is collected by a national network of processors and brokers. The scrap is visually inspected and graded. Chemical analyses are performed when necessary. Loose scrap is baled and stored until needed. Alloy scrap is segregated and identified by the alloy and the impurity content of each batch. Scrap of unknown composition may be melted and analyzed to determine its chemistry (CDA 1998a). The major processes involved in secondary copper recovery are scrap metal pretreatment and smelting. Pretreatment prepares the scrap copper for the smelting process. Smelting is a pyrometallurgical process used to separate, reduce, or refine the copper.

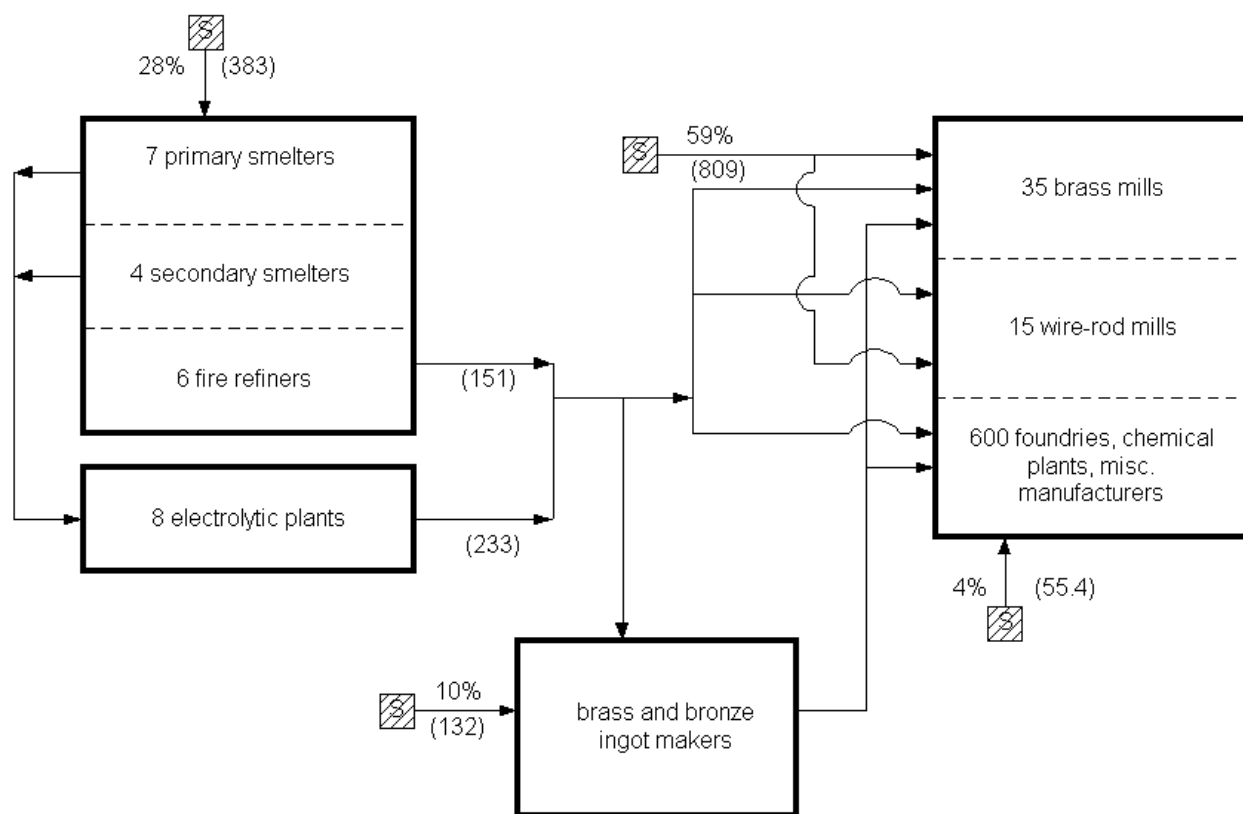


Figure C-1. Simplified flow diagram for copper-base scrap in 1997. Units are percent of total copper consumed from copper-base scrap and metric tons (in parentheses).

Pretreatment includes cleaning, and concentrating the scrap materials to prepare them for the smelting process. Pretreatment can be accomplished by: (1) concentration, (2) pyrometallurgical, or (3) hydrometallurgical methods. These methods may be used separately or combined. Pretreatment by concentration is performed either manually or mechanically by sorting, stripping, shredding, or magnetic separation. The resulting scrap metal is then sometimes briquetted in a hydraulic press. Pretreatment by the pyrometallurgical method includes sweating, burning of insulation (especially from scrap wire), and drying (burning off oil and volatiles) in rotary kilns. The hydrometallurgical method includes flotation and leaching with chemical recovery. After pretreatment the scrap metal is ready for smelting (U.S. EPA 1995).

Table C-3. Copper Recovered from Scrap Metal Processed in the United States in 1997

Scrap			Amount (t)
Kind of Scrap	New Scrap	Copper-base	909,000
		Aluminum-base	46,800
		Nickel-base	91
		Zinc-base	—
		Total	955,891
	Old Scrap	Copper-base	465,000
		Aluminum-base	30,300
		Nickel-base	28
		Zinc-base	19
		Total	495,347
	Grand total		1,451,238
Form of Recovery	As unalloyed copper	At electrolytic plants	233,000
		At other plants	161,000
		Total	394,000
	As alloys and compounds	Brass and bronze	979,000
		Alloy iron and steel	743
		Aluminum alloys	77,500
		Other alloys	113
		Chemical compounds	252
		Total	1,057,608
	Grand total		1,451,608

Source: Edelstein 1998

Note: Totals differ due to round-off errors.

C.2.3 Copper Refining Operations

Copper scrap is utilized by both primary and secondary producers of copper. Locations in the copper refining process where copper scrap may be introduced are summarized in Figure C-2. This diagram does not address the large amount of copper-alloy scrap, which is used by brass mills, ingot makers, and foundries. Based on the data in Table C-4, the figure illustrates the disposition of 63% of old scrap. In this figure, typical secondary copper operations are described by the dashed boxes.

Secondary smelters use several processes that are equivalent to those employed as primary pyrometallurgical processes for mined copper ores. A first stage smelting process is most commonly performed in either a blast furnace, reverberatory furnace, or an electric furnace. This is followed by treatment in a converter furnace and then in an anode furnace. The copper may be further purified by electrolytic refining. Depending on the grade, copper scrap may enter the flow stream at numerous locations. Some slag from the process is sold or landfilled; the remaining slag is recycled back into the smelting furnace because of its copper content. Sulfur dioxide, a by-product gas from *primary smelting*, can be collected, purified, and made into sulfuric acid for sale or for use in hydro-metallurgical leaching operations. Each of the major processes used in recycling copper scrap is described below.

Table C-4. Copper Consumption from Copper-Base Scrap in the United States in 1997 (t)

Type of Operation	From New Scrap	From Old Scrap	Total
Brass/bronze ingot makers	35,200	96,500	132,000
Copper refineries	91,400	292,000	383,000
Brass and wire-rod mills	771,000	32,800	804,000
Foundries and manufacturers	11,200	43,900	55,100
Chemical plants	252	—	252
Total	909,052	465,200	1,374,352

Note: Totals differ due to round-off errors.

C.2.3.1 Copper Smelting Practices

Blast Furnace

The vertical shaft furnace, also known as the blast furnace or cupola, has the ability to smelt copper-bearing material of an extremely diverse physical and chemical nature. It is the unit that is commonly employed in the pyrometallurgical treatment of low-grade secondary copper material and largely controls the metal losses in the system (Nelmes 1984).

Low-grade copper scrap containing skimming, grindings, ashes, iron-containing brasses, and copper residues is typically smelted in a blast furnace, where coke is added as a reductant and limestone is added to assist in forming a calcium-iron-silicate slag. The molten “black copper” product from the blast furnace is transferred via a ladle to a converter for further purification. It is then fire refined and electrorefined. Dusts from the blast furnace are collected in a baghouse.

C-12

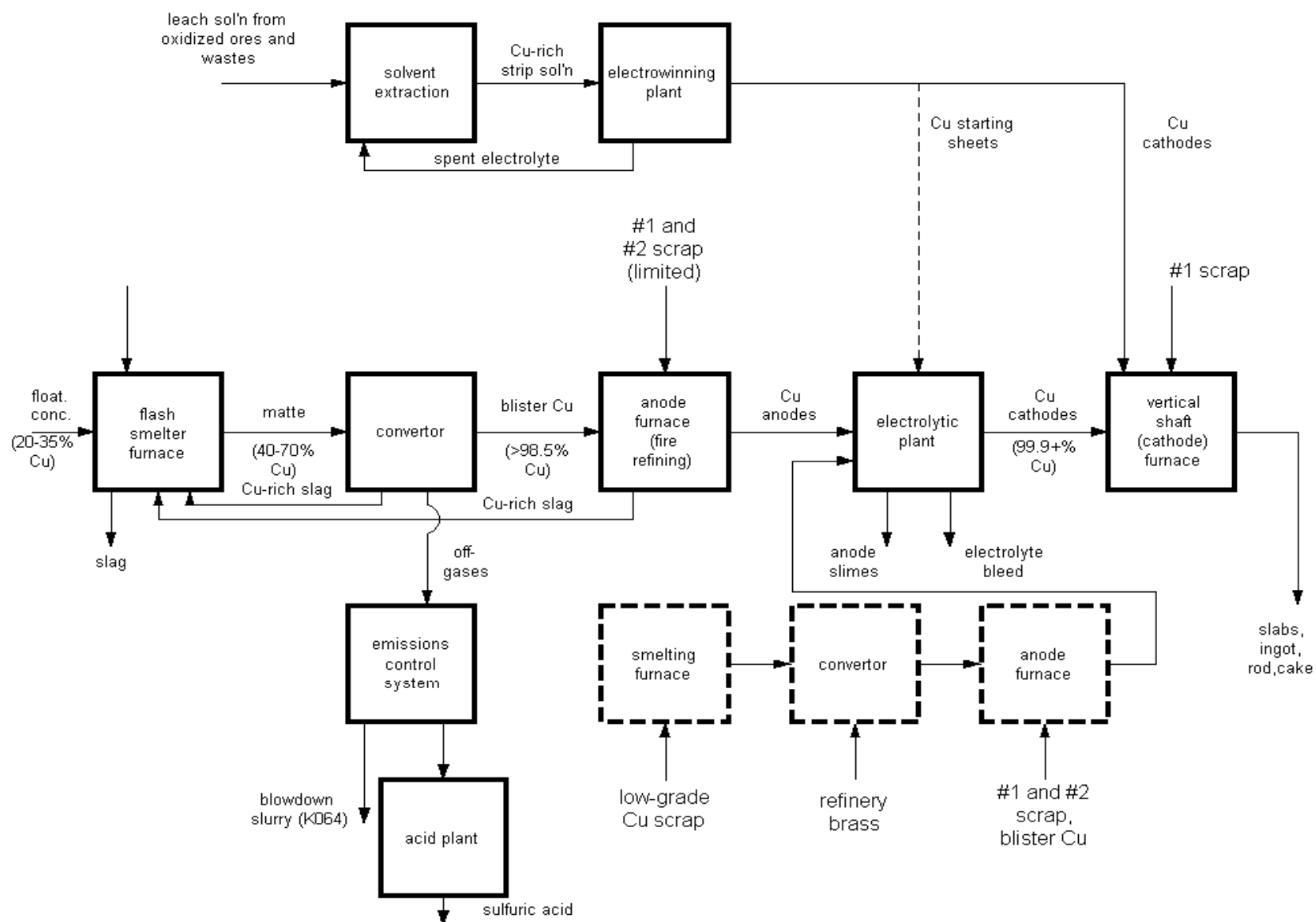


Figure C-2. Process diagram for the flow of copper scrap in primary and secondary copper refining. (Dashed boxes represent secondary processor's operations.)

The ranges of compositions for blast furnace process streams, as reported by several authors, are summarized in Table C-5. The feed to the cupola described by Opie et al. (1985) contained about 30% copper. The average dust composition from a cupola has also been reported by Garbay and Chapuis (1991):

- Cl 3%
- Cu 4%
- Zn (ZnO) 55%
- Sn 4%
- Pb 9%

The dust composition, which is typical of French smelting practice, is encompassed by the ranges of values in Table C-5.

Table C-5. Composition of Process Streams from the Smelting of Copper Scrap in a Cupola Blast Furnace (%)

Item	Black Copper			Slag		Dust		
	Kusik and Kenahan	Nelmes	Opie	Nelmes	Opie	Kusik and Kenahan	Nelmes	Opie
Cu	75 - 88	80	65 - 70	0.9	1.5 - 2	0.1	1.5	8 - 12
Ni		4	7.5 - 12	1.5	1 - 1.5			0.1 - 0.5
Sb	0.1 - 1.7		0.5 - 1.5		1 - 2	0.1		0.3 - 0.8
Sn	1.5	4	2 - 4	0.3	1 - 2	5 - 15	1	1.5 - 2
Fe	3 - 7	5	5 - 10	30	30 - 35			
Zn	4 - 10	3	2 - 4	3	2 - 4	58 - 61	50	20 - 35
Pb	1.5	4	2 - 4	0.6	1.5 - 3	2 - 8	15	13 - 15
SiO ₂				27				4 - 7
Cl						0.1 - 0.5		6 - 10
F								1 - 5
CaO				14				
Al ₂ O ₃				9				
Other		<1		15			32.5	

Sources: Kusik and Kenahan 1978, Nelmes 1984, and Opie et al. 1985.

During the blast furnace smelting operation, the scrap charge is fed onto a belt conveyer, which in turn discharges into one of two skip hoist buckets (Browne 1990). These buckets are hoisted and alternately dumped into opposite sides of the furnace. Coke is added as a reducing agent along with silica, lime, or iron oxide. Air is injected by means of tuyeres. The copper-bearing material initially enters at the top of the furnace into a zone at 400-600°C. It subsequently descends into the tuyere zone and increases in temperature to about 1,400°C⁵ (Schwab 1990). According to Nelmes (1984), many secondary copper blast furnaces have an area of about 35 ft² with the range being from 12 to 140 ft². Assuming a melting rate of 6 tons/ft²/day, a typical blast furnace would have an output of 210 tons/day.

A mixture of molten copper and slag flows down a launder into an oil-fired rocking furnace that can rotate. This furnace is large enough to give the slag sufficient time to separate from the copper. Rotating the furnace in one direction allows the liquid copper to fill a preheated ladle on a rail car below the rocking furnace. Rotation in the opposite direction allows the slag to pour into a granulating trough. Granulation is accomplished by impinging the liquid slag with a high pressure jet of water. The slag and water are collected in a pit that is large enough to remove the slag with a clamshell bucket on a crane.

When granulated blast furnace slag is dried, crushed, and screened, it is used to manufacture a variety of commercial products. It is useful for making a variety of abrasives, filler for asphalt shingles, roofing sealers, grit for sand blasting, road surface bedding, and in the manufacturing of mineral wool and light-weight cement aggregates (Nelmes 1984, Schwab 1990, Mackey 1993). The metal content of the slag is typically 1% copper or less (Mackey 1993). Some slag is stored or discarded in piles on site (U.S. EPA 1995).

In some cases the slag may be treated for recovery of additional metal values prior to granulation. Opie et al. (1985) describe a processing step in which the blast furnace slag is pyrometallurgically treated in an electric arc furnace with 2% coke added as a reductant. The arc furnace temperature is 100 to 200°C higher than in the blast furnace. A small amount of additional black copper is produced, dust is collected in a separate baghouse, and a slag with reduced metal values is obtained. The composition ranges for these products are presented in Table C-6 and are based on treating the blast furnace slag described by Opie et al. (1985) (see Table C-5).

⁵ The melting point of pure copper is 1,083°C.

Table C-6.
Composition of Products Obtained from Treating Copper Blast Furnace Slag in an EAF

Element	Black Cu (%)	Final Slag (%)	Baghouse Dust (%)
Cu	55 - 60	0.2 - 0.5	1 - 2
Ni	5 - 10	0.2 - 0.4	0.2 - 0.3
Sb	0.5 - 1.5	0.1 - 0.20	0.1 - 0.2
Sn	2 - 4	0.05 - 0.1	1.5 - 3.0
Fe	5 - 7	30 - 35	0.5 - 0.7
Zn	1.5 - 2.0	0.5 - 1.0	45 - 55
Pb	1.0 - 1.5	0.5 - 1.0	15 - 20

Source: Opie et al. 1985

For a 100-ton blast furnace charge consisting of copper scrap, coke, and slagging agents, the expected output is 40 tons of black copper, 40 tons of slag, and 5 tons of baghouse dust (Nelmes 1984). Carbon in the charge is converted to CO/CO₂, which is exhausted through a stack. The overall elemental partitioning for a copper blast furnace, based on these mass partitioning values and the elemental compositions included in Table C-5, is presented in Table C-7.

Table C-7. Partitioning During Blast Furnace Smelting of Copper Scrap (% recovery)

Output	Cu	Sn	Fe	Zn	Pb	Ni	Al ₂ O ₃	CaO	SiO ₂
Metal	98.64	90.4	14.29	24.49	61.78	63.9	--	--	--
Dust	0.25	2.82	--	51.02	28.96	--	--	--	--
Slag	1.11	6.78	85.71	24.49	9.26	36.1	100	100	100

Source: Nelmes 1984

Table C-7 does not include 1.6 tons of “Other” material reporting to the dust and 6.0 tons reporting to the slag.

Reverberatory Furnace

Reverberatory furnace smelting began in the nineteenth century. It still accounts for a significant fraction of both primary and secondary copper production and recycling of secondary scrap metal. Disadvantages of these furnaces are the long melting cycle times and low fuel efficiencies (Davenport 1986).

In a reverberatory furnace, the scrap copper is charged into one or more piles located behind one another, in front of several high capacity end-wall-fired burners. These high capacity conventional burners typically are fired above the copper scrap and use the reverberatory effect for heat transfer, i.e., re-radiation from the refractory roof and walls to the scrap. During the melting cycle, when the process requirements for energy are high, the surface of scrap exposed to the flame radiation and to radiative heat transfer from the furnace refractory surfaces is small relative to the total surface area of the scrap. This is because the top layers of scrap shade the interior scrap surfaces from the radiation, resulting in low rates of radiative transfer to the entire scrap charge. In addition, convective heat transfer to the interior of the scrap charge is limited by low circulation of gases within the scrap.

A typical reverberatory furnace is charged with approximately 250 tons of scrap and about 100 tons of liquid metal in order to maintain a 24-hour operating cycle; the melting portion of the cycle is 8 hours. This represents an average “melt-in” rate of cold scrap of about 31 tons per hour (Wechsler and Gitman 1991). The reverberatory furnace is charged by fork-lift trucks or by charging machines. Impurities are removed during melting by air oxidation and skimming away the resultant slag. The oxygen content of the melt is then reduced to the desired level (e.g., 0.03% to 0.04%) by adding a hydrocarbon source (e.g., natural gas) and the copper is cast into shapes such as cakes, billets, or wire-bar.

In some cases melting of copper scrap in a reverberatory furnace may be the only step in the refining process. At Reading Tube Co., for example, No. 1 copper scrap is the sole feed. All of the incoming scrap is visually inspected for known forms of suspect copper. An in-depth visual inspection is made of selected samples from the scrap; chemical analyses are taken from samples to screen for impurities. (The scrap is not monitored for radioactivity.) The scrap is charged into a 200-ton reverberatory furnace,⁶ melted, and blown with air or oxygen to oxidize impurities. The oxide slag is skimmed from the melt. The melt is covered with charcoal and “poled” to remove oxygen. In the poling process, green hardwood logs are thrust into the molten copper bath, where the hydrocarbons react with the oxygen to form CO/CO₂. The molten copper is then laundered. In this process the copper flows under charcoal into a ladle which is covered with a carbon-based product. The laundering removes additional oxygen from the melt. Final deoxidation is promoted by the addition of phosphorus; the melt is cast into billets for subsequent

⁶ One heat per day is typically produced. The furnace undergoes an annual maintenance shutdown. Reading also operates a shaft furnace, which can produce 100 tons per day.

fabrication into tubing (Reading 1999). The slag is sold to an outside processor for recovery of additional copper values. Offgases from the furnace pass through an after-burner to convert CO to CO₂ and to destroy any hydrocarbons; they are then exhausted through a stack. Stack offgas is monitored for total particulates, opacity, and SO₂.

Electric Arc Furnace

The electric arc furnace (EAF) is also used in secondary copper smelting <<http://www.halstead.com>> (5/26/99). At Halstead Industries (now part of Mueller Industries, Inc.) in Wynne, Arkansas, bales of copper scrap, cathode sheets, or copper ingots (from Codelco in Chile) are preheated with natural gas to about 1,000°F and charged into a 16,000-volt EAF⁷. In the EAF, the copper is melted and heated to between 2,200-2,300°F and then poured into a graphite-covered launder at a rate of 640 pounds per minute. Phosphorus pellets are added to the molten copper stream for deoxidation⁸. The copper flows from the launder to the casting machine, where four logs, each 9 inches in diameter and 25 ft long, are simultaneously cast at a rate of about 8 inches of ingot length per minute. The logs weigh 6,160 lb each. The launder then swings to a second set of molds while the logs produced from the first set of molds are raised from the casting pit under the molds and transferred with an overhead crane to the billet cutter. At the billet cutter each log is sawed into 14 extrusion billets, each 20.25 inches long and weighing 420 lb.

The EAF is rated at 72 tons and produces 310 to 330 tons per day (Blanton 1999). The charge is 75% to 80% scrap and 20% to 25% cathodes or ingots. Incoming scrap is screened with a Geiger counter for radioactivity. Plant procedures call for an alert at twice background and automatic rejection of the shipment at three times background. In the past four to five years there have been two alarms, both traceable to truck drivers who had been treated with radioisotopes. The furnace is equipped with a baghouse for dust collection. The dust generation rate is about 5 lb/ton and the dust contains 73% to 76% copper, some zinc, small amounts of iron and tin, and about 0.1% to 0.15% lead. Significant carbon, attributable to melt poling, is also present. Slag is skimmed from the furnace using hand rakes. The slag contains 30% to 50% copper, considerable carbon,

⁷ Mueller Industries also has smelting facilities in Fulton, Mississippi where, until recently, all melting was done in a shaft furnace. They have now added a Maerz reverberatory furnace at that production location.

⁸ The alloy produced is C12200 or Phosphorus-Deoxidized High Residual Phosphorus Copper, containing 99.9% copper (min.).

calcium from bone ash (a slagging agent), zinc, and iron oxide. Both the baghouse dust and the slag are sold to Chemetco for further processing. A metric for slag generation was not available.

C.2.3.2 Copper Converting

The product from the smelting furnace may contain significant amounts of Fe, Sn, Pb, Zn, Ni, and S. These elements are removed either by reduction and evaporation or by oxidation. At smelting temperatures, oxides of most metals are more stable than CuO or Cu₂O. Thus, from an equilibrium thermodynamics perspective, these metals would be transferred to the slag under oxidizing conditions. Impurity metals with high vapor pressures (e.g., Pb, Cd, Zn) or with high-vapor-pressure oxides (e.g., SnO, Cs₂O, P₂O₃) may volatilize and be collected in the zinc-rich dust. Tin is recovered from baghouse dust and used as tin/lead alloy for solder, and zinc is recovered and converted to ZnO for the pigment industry (Göckman 1992).

The conversion process employs either a Peirce-Smith converter or a top blown rotary converter (TBRC). Oxygen-enriched air or pure oxygen is used for the removal of impurities (Davenport 1986; Roscrow 1983).

The charge is melted under reducing conditions to avoid premature oxidation of copper. Lead, tin, and zinc are also reduced to metals. Zinc-rich dust is collected in a baghouse. Iron reacts with silica flux to form a silicate slag.

The furnace is then run in an oxidizing mode using air or oxygen. The remaining iron, zinc, tin and lead are removed. When processing black copper produced from scrap in a converter, the converter must be “blown hard” to remove nickel, tin, and antimony from the melt. This results in a slag containing over 30% copper. The slag is returned to the blast furnace for copper recovery (Opie et al. 1985). The resultant converter product is blister copper (~96% Cu). A typical furnace can produce from 4,000 to 15,000 tons per year of blister copper (O’Brien 1992). Based on metal content, the baghouse dust may be shipped to zinc smelters or to tin and lead refiners for metal recovery.

The composition of the blister copper, the slag, and the baghouse dust from a converter operation based on secondary copper smelting is summarized in Table C-8.

Table C-8. Composition of Converter Products from the Smelting of Copper Scrap (%)

Element	Blister Copper	Slag	Baghouse Dust
Cu	94 - 96	30 - 35	2 - 3
Ni	0.5 - 1.0	10 - 15	0.5 - 1.0
Sb	0.1 - 0.3	0.5 - 1.5	0.5 - 1.5
Sn	0.1 - 0.2	2 - 4	10 - 20
Fe	0.1 - 0.3	20 - 25	0.5 - 1.0
Zn	0.05 - 0.1	1.0 - 1.5	25 - 35
Pb	0.05 - 1.0	2.5 - 4.0	20 - 25

Source: Opie et al. 1985

C.2.3.3 Fire Refining

The blister copper from the converter is then processed in an anode furnace, which is generally some type of reverberatory furnace. Anode production is the last processing step prior to electrolytic refining and is called “fire refining.” Sulfur and other readily oxidizable elements are removed by air oxidation. The dissolved oxygen is then removed from the melt by reaction with hydrocarbon gases prior to anode casting. During fire refining, the melt is first saturated with O₂ (about 0.8 to 0.9% O) and the oxygen is then decreased to about 0.2%. Oxidized impurities are collected in the slag, which is recycled either on-site or at another refinery.

The anodes are then cast in copper molds on a rotating horizontal wheel. Anode thickness is controlled by weighing the copper poured. The anodes contain about 99.5% copper with impurities such as Ag, As, Au, Bi, Fe, Ni, Pb, Sb, Se, and Te (Kusik and Kenahan 1978, Davenport 1986). Garbay and Chapuis (1991) list the composition of fire-refined anodes produced from a French smelting operation in a 250-t reverberatory furnace, as listed in Table C-9.

Schloen (1987) summarized typical anode chemistries at nine U.S. electrolytic copper refineries which were operating at the time. Results of this survey are presented in Table C-10.

C.2.3.4 Electrolytic Refining

The final stage in copper purification employs an electrolytic refining process that yields copper which may contain less than 40 ppm of metallic impurities (Ramachandran and Wildman 1987).

During electrorefining, copper anodes and pure copper cathode starter sheets are suspended in a $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte, through which an electrical current is passed at a potential of about 0.25 Vdc. The electrolytic refining process requires 10 to 14 days to produce a cathode weighing about 150 kg. During electrolysis the copper dissolves from the anode and deposits on the cathode. Impurities such as Au, Ag, and other precious metals, as well as Pb, Se, and Te collect in the anode slimes⁹. These anode slimes are collected and sent to a precious metals refinery (Davenport 1986). Other elements such as Fe, Ni, and Zn dissolve in the electrolyte¹⁰ and are removed from the copper electrolysis cells in a bleed stream. The bleed stream is sent to “liberator” cells, where the solution is again electrolyzed and soluble copper is plated out on insoluble lead anodes. The bleed stream is then treated for NiSO_4 recovery by concentrating the solution in evaporator vessels, where NiSO_4 crystals precipitate. The remaining liquor is called “black acid.” Both the NiSO_4 and the black acid are typically salable products (Kusik and Kenahan 1978).

Table C-9. Composition of Anodes Produced in a 250-t Reverberatory Furnace (ppm)

Ag	600	Sn	400	Bi	20
As	1,110	Sb	250	Fe	50
Pb	2,200	Se	100	Zn	100
Ni	500	Te	100	S	10

Source: Garbay and Chapuis 1991

Note: Balance Cu

The processing conducted at the ASARCO's Amarillo copper refinery (Ramachandran and Wildman 1987) is illustrative of electrorefining operations. Blister copper is shipped to the refinery in solid bottom gondola rail cars, which are unloaded either in a storage area or at the Anode Casting Department. Blister copper from the storage area is transferred to the Anode Casting Department via 11-ton fork lifts. Usage of blister copper is 8,500 tons per month (tpm). Number 2 copper scrap is received loose in box cars or trucks. The scrap is sampled and briquetted into bales which measure about $40 \times 36 \times 17$ inches. Scrap usage is up to 6,000 tpm. The blister copper and the scrap are melted in a 350-ton Maerz tilting reverberatory furnace,

⁹ According to U.S. patent 4,351,705, a typical slimes composition is 5-10% Cu, 4-8% Ni, 6-8% Sb, 15-25% Sn, 5-12% Pb, 0-2% Ag, and 4-8% As.

¹⁰ According to Davenport (1986), As, Bi, Co, Fe, Ni, and Sb report to the electrolyte.

which operates on a 22-hour cycle. Copper for anodes, each weighing about 765 pounds, is poured into molds in a casting machine. The finished anodes are transferred to the tankhouse with a 20-ton straddle carrier. The refinery also uses a 50 ton per hour shaft furnace to remelt anode scrap from outside sources and reject anodes. Output from the shaft furnace is transferred to a 15-ton holding furnace, which feeds the same casting wheel as used with the reverberatory furnace. Monthly anode production is about 22,000 tons. Typical anode chemistry is:

• Cu	98.6 - 99.4%
• Ni	0.04 - 0.08%
• Sb	0.05 -0.08%
• As	0.03 - 0.09%
• Se	0.06 - 0.07%

The tankhouse contains six independent modules, each with its own rectifier, circulation system, reagent system, and operating crew. Each module contains 400 cells. The annual output of the plant is about 460,000 tons. Additional anodes required to maintain tankhouse operation at capacity are obtained from external sources.

A typical analysis of the cathode copper is:

• Cu	99.96%
• S	6 ppm
• Se	<1 ppm
• Sb	1 ppm
• As	1 ppm
• Bi	0.2 ppm
• Fe	2 ppm
• Nickel	2 ppm
• Pb	<1 ppm
• Sn	<1 ppm
• Zn	< 3ppm

Table C-10. Anode Compositions at Various U.S. Electrolytic Copper Refineries

Element/ units	AT&T Nassau Metals Gaston, S.C.	Cerro Copper Products Co. East St. Louis, Ill.	Copper Range Co. White Pine, Miss.	Kennecott Refining Corp. Baltimore	Kennecott Utah Refinery Bingham Canyon, Utah	Magma Copper Co. San Manuel, Ariz.	Phelps Dodge Refining Corp. El Paso, Tex.	Southwire Copper Division Carrollton, Ga.	ASARCO Amarillo Copper Refinery Amarillo, Tex.
Cu %	99.2	99.6	99.5-99.8	99.63	99.6	99.78	99.5	99.3	99.3
Ag ppm	120	210	700	435	403	175	225-300	600	1,200
Se ppm	50	20	25	490	500	415	200-450	--	600
Te ppm	50	130	--	69	140	6	25-50	20	100
As ppm	50	100	200	500	560	24	25-50	500	400
Sb ppm	350	80	50	210	50	73	35-50	700	550
Bi ppm	50	20	5	41	33	3	5-15	30	45
Pb ppm	1,500	1,600	80	380	140	63	15-150	1,000	500
Ni ppm	1,500	500	150	510	220	121	100-700	3,000	1,700
O ₂ ppm	2,000	1,200	1,000-1,500	1,228	1,960	900-1,200	1,400-2,800	2,000	1,600

Source: Schloen 1987

A continual bleed of electrolyte is taken from the electrorefining cells to a separate building containing copper-removal cells. Here the copper is passed through a number of primary liberator cells plumbed in series, where the copper content of the electrolyte is reduced from 40 to 20 g/L. The cathodes from these primary cells are returned to the Anode Casting Department for recasting into new anodes. A portion of the partially purified liquor is returned to the main tankhouse and the balance is sent to secondary recovery cells, where the copper content of the electrolyte is further reduced to about 1 g/L. The cathodes from the secondary cells may be returned to the Anode Casting Department or shipped to a smelter in El Paso, Texas for reprocessing.

The treated electrolyte, which contains 15 - 20 g/L of Ni, is processed through one of two submerged combustion evaporators to produce NiSO_4 . A single evaporator can produce about 115 tpm of NiSO_4 on a dry-weight basis¹¹. The black acid remaining after nickel removal is either returned to the tankhouse for use in acid makeup or is used to leach the slimes. The crude nickel sulfate, which contains about 5% H_2SO_4 and 3% H_2O , is shipped to nickel producers. Slimes are processed at the electrorefinery.

C.2.3.5 Melting, Casting, and Use of Cathodes

The cathodes are washed, melted, and cast into shapes for fabrication and use. The melting is usually done in a vertical shaft furnace in which stacks of cathodes are charged near the top and melt as they descend, heated by combustion gases. The operation is continuous, and the molten copper may be cast and rolled to form rod for wiremaking, or into slabs and billets for other wrought products.

C.2.3.6 Slag Handling

The slags from the copper converters and the anode furnaces are rich in copper and are returned to the smelting furnace for recovery of additional copper values. The smelting furnace slag is stored or discarded in slag piles on site. Some slag is sold for railroad ballast and for blasting grit (U.S. EPA 1995). Most of the radioactive contaminants would end up in the slag because they tend to be more easily oxidized than copper.

¹¹ If the plant processes 460,000 tons of copper anodes containing 0.08% Ni and produces 92% NiSO_4 , the nickel sulfate production would be about 88 tpm if all the nickel forms NiSO_4 , which in turn contains 38% Ni by weight.

C.2.3.7 Offgas Handling

Offgases from the converters at primary producers are collected by a hood system and processed through an emission control system, which typically consists of an electrostatic precipitator (ESP) and a wet scrubber¹². The scrubbed gas is processed through an acid plant and converted to sulfuric acid. Since secondary producers do not handle high sulfur matte, they do not have acid plants in their systems.

C.2.3.8 Illustrative Secondary Smelter

Operations at the Southwire Company in Carrollton, Ga. are briefly described to indicate the complexity and variability of the operations at a large secondary refiner. Examples of the types of scrap handled by Southwire include blister copper, spent and reject anodes, No. 1 copper scrap, No. 2 copper scrap, No. 3 copper scrap, and miscellaneous copper-bearing materials (e.g. bronze, brass, and small motors) www.southwire.com/copper/recovery.htm (2/24/99).

Southwire has a fixed NaI scintillation detector system built by Eberline to monitor incoming trucks for radioactive contamination. The system has alarmed three or four times—once by radon in propane from a Texas salt dome (McKibben 1999).

Southwire uses a blast furnace to process low-grade scrap, a top-blown rotary converter to process the blast furnace output into blister copper, a reverberatory furnace to melt No. 2 scrap, and a shaft furnace to melt and refine blister copper and No. 1 scrap and produce anodes. The high copper slags from the other furnaces are returned to the blast furnace for the recovery of additional metal values. The blast furnace slag is granulated, dried, and screened. It is sold to the roofing industry for use in shingles (Gerson 1999). The Southwire flowsheet is shown in Figure C-3 (McDonald 1999).

The brick plant in Figure C-3 was scheduled to be replaced by a new central mixing facility (Capp 1997). In the new facility, baghouse dust from the Maerz reverberatory furnace, the anode shaft furnace, the anode holding furnace, and the slag plant are collected in dust-tight tote bins. When the tote bins are full they are transported by fork-lift truck to the central mixing facility. Tote bins are filled approximately once per 12-hour shift from the reverberatory furnace

¹² While some sources have suggested that scrubber blowdown at primary copper facilities is RCRA-regulated waste (K064), this is not the case. In a 1990 decision, a federal district court remanded the K064 listing to EPA for reconsideration. No further action has been taken by the Agency. The wastes may be characteristically hazardous due to acidity or metals content.

baghouse, once per shift from the slag plant baghouse, and once every one to three days from the other sources. Dust is transported from the tote bin via an enclosed screw auger to a 200 ft³ storage silo (called a day bin), which holds about a three-day inventory. The dust is then moved by a second enclosed screw auger to an agglomeration unit with a design capacity of 20 tons per hour (tph), where water is added and a paste is produced. This paste is transferred to a wet bin for storage until the product is needed for feed to the blast furnace. When required, the paste is moved with a front-end loader to the blast furnace charge beds, where it is blended with other feed materials. The central mixing facility has an annual design input of about 51,100 tons per year (TPY) of baghouse dust. The facility design calls for limiting emissions through two low stacks (18 and 20 feet above grade) to 1.64 tpy of particulate material with the following indicated contaminants:

• As	0.07 tpy
• Cr	0.05 tpy
• Se	0.05 tpy
• Cd	0.004 tpy
• Ni	0.004 tpy
• Sb	0.000 tpy
• Co	0.000 tpy
• Mn	0.000 tpy
• Be	0.000 tpy

These estimates were based on the analysis of baghouse fines.

Each furnace has at least one baghouse and some have a backup. Dust from the blast furnace is disposed of in a hazardous waste landfill because of Cd, Pb, and other heavy metals. Dust from the converter is sold to an overseas customer, who recovers metal values such as Pb, Sn, and Zn. Dust from the reverberatory furnace and the shaft furnace is returned to the process as described above. It is difficult to obtain a figure of merit for dust generation because it varies significantly with the type of scrap being processed. For example, a high-brass furnace charge will generate more zinc dust.

COPPER WIRE MANUFACTURING

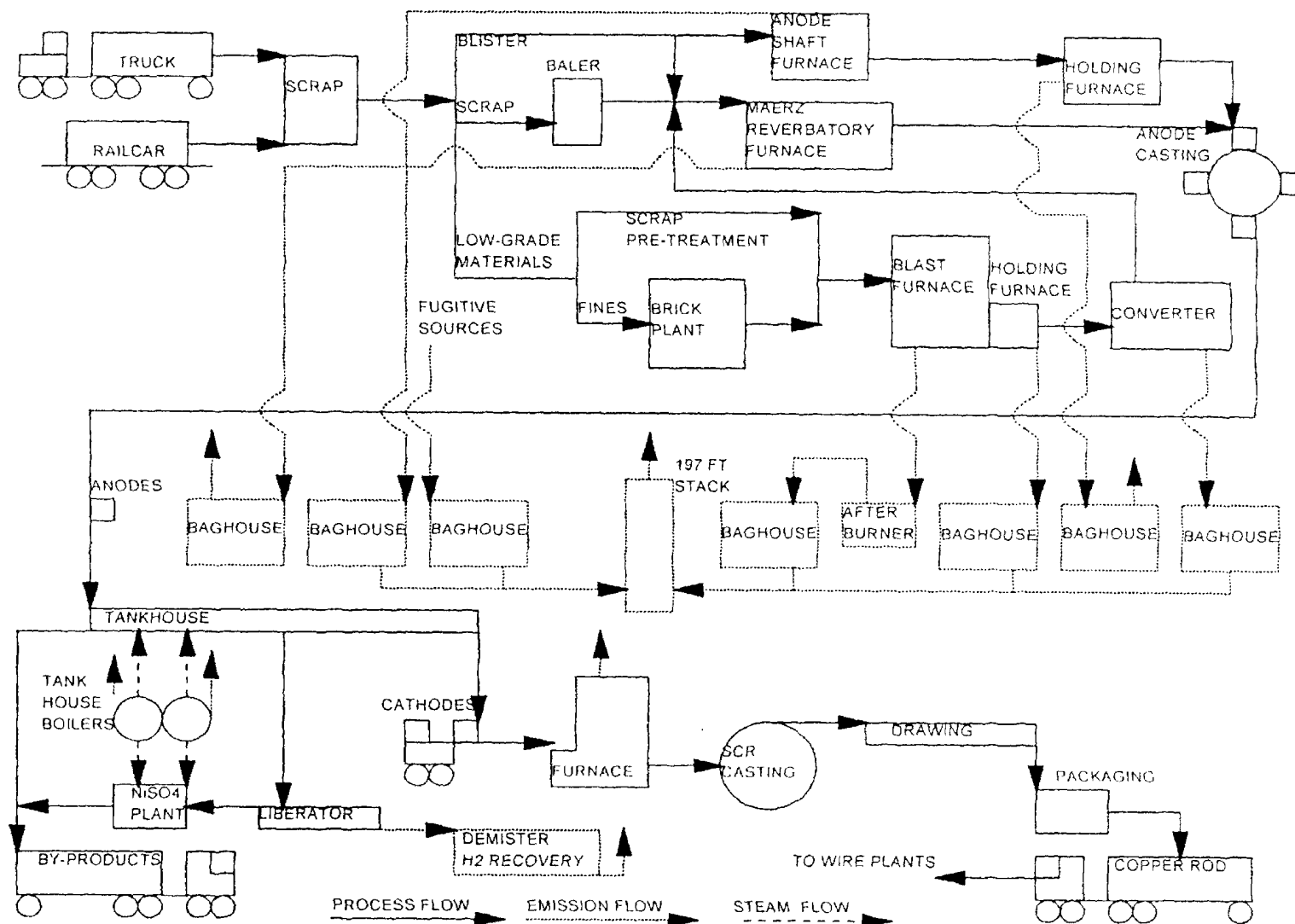


Figure C-3. Flow Diagram of the Copper Division of Southwire (CDS)

Anodes are electrolytically refined. The anode slimes are sold to an offshore processor for precious metal recovery. Copper is removed from the electrolyte bleed by electroplating. The solution is then evaporated. Nickel sulfate is crystallized and recovered for sale.

Cathodes from the electrorefining operation are melted in a shaft furnace and cast into copper rod. In 1998, the output of the rod-mill shaft furnace was about 342,000 tons (McDonald 1999).

Operations at Chemetco, a secondary smelter in Hartford, Illinois are somewhat different. Chemetco has four 70,000 lb reverberatory furnaces and four top-blown rotary converters to process scrap (Riga 1999). They process scrap ranging from high-grade copper wire to low-grade slags and skims. Slags are sold for railroad ballast, road beds, and asphalt shingles. Anodes are sold to Asarco for electrorefining.

C.2.4 Brass and Bronze Ingot Production

As shown in Figure C-1, about 10% of copper-base scrap is consumed by brass and bronze ingot makers. At the ingot manufacturer, scrap is melted in a reverberatory furnace. Fluxing agents such as borax and sodium nitrate are added. Alloying agents such as tin may also be included in the furnace charge. Zinc evolved in the melting process is collected in a baghouse. Slag is either returned to a smelter for reprocessing or shipped for disposal (Kusik and Kenahan 1978).

Aluminum bronze is melted in gas- or oil-fired crucible furnaces, coreless induction furnaces, or in reverberatory furnaces (for very large castings) (U.K. CDA 1999). The furnace charge typically involves addition of cathode copper, aluminum (either as ingot or a 50% Al-50% Cu master alloy), and iron and nickel (either in elemental form or as a master alloy). Process scrap is generally added when the ingots are remelted to produce the final castings but may be added at the end of the alloying schedule. During melting, most of the copper together with the iron and nickel are introduced into the furnace under a charcoal blanket and the melt is heated to about 1,300°C. The remaining copper is then added, the charcoal is removed and the aluminum is charged. A small amount of cryolite or fluoride flux is then stirred into the melt to clean entrapped metal from the dross before pouring the melt into ingot molds.

C.2.5 Brass Mills

Brasses are alloys of copper with up to 40% zinc. Other alloying elements such as Al, Fe, Mn, Pb, and Sn may be added at levels of up to a few percent of each metal, depending on the specific

alloy being produced. As shown in Table C-11, brass mills are major consumers of yellow and red brass scrap. An example is the Chase Brass and Copper Company, which produces brass rod primarily from scrap. Chase currently has an annual capacity of about 300 million lb per year and is expanding to 400 million lb per year. The scrap is melted in four induction furnaces and cast into logs, which are 23 ft long and 10 inches in diameter. About 80% of their scrap requirements are obtained through purchase and tolling arrangements with their customers. In 1997 there was a price differential of 5 cents per pound between the metal selling price to the customer and the metal buying price (i.e., the scrap price) from the customer. The balance of their requirements are purchased from scrap dealers at the free-market price. Chase uses hand-held detectors to check scrap from unknown (i.e., open-market) sources for radioactivity. They have had no instances where any activity has been detected in the scrap. Several million pounds are typically in inventory at the plant site. A baghouse system is used to collect dust from the furnace offgas. Dross is removed from the furnace and run through a vibratory screening system to collect metal for internal recycle. Both the undersize from the dross processing and the baghouse dust are drummed and sold to an off-site reprocessor (Warner 1999, Woodserman 1999). The reprocessor treats these waste streams with mineral acids and then crystallizes various metal salts from the solutions. Typically, the salts are sold to the steel industry for use in fluxes. Chase seldom uses copper scrap in its melting operations. Use of copper in the furnace charge requires a higher melting temperature, which increases zinc losses from the melt. Chase does not have a figure of merit for baghouse dust production. The value is quite variable depending on the alloy being melted, the quantity of scrap in the furnace charge, etc.

Olin Brass in East Alton, Ill. produces 60 to 70 different copper and brass alloys. Most of the scrap used is either run-around (internal) scrap or customer returns (either direct or handled by a broker). A portable spectrometer may be used to check the chemistry of an incoming truckload of scrap. Occasionally, pure copper is used for selected products. Melting is done in small induction furnaces that feed a large holding furnace. The furnace charge is typically baled scrap. Most Olin alloys are cast by the direct chill method, in which multiple ingots are cast simultaneously. Each rectangular cross-section ingot is about 25-ft long and weighs 18,000 lb. The ingots are reduced to sheet and strip via a series of hot and cold rolling operations (Olin 1995). Furnace offgas is processed through cyclone separators and a baghouse. During melting, dross formation is not intentionally promoted. However, use of highly reactive alloying additions may enhance dross formation. Dross disposition practices, which are proprietary, are designed to maximize process economics (presumably by using some sort of recycling). The same considerations apply to treatment of baghouse dust (Shooter 1999).

Table C-11. Consumption of Copper-Base Scrap in 1997

Scrap Type and Processor	Consumption (t)
No. 1 wire and heavy:	
Smelters, refiners, and ingot makers	149,000
Brass and wire-rod mills	413,000
Foundries and misc. manufacturers	35,800
No. 2 mixed light and heavy:	
Smelters, refiners, and ingot makers	230,000
Brass and wire-rod mills	34,900
Foundries and misc. manufacturers	2,770
Total unalloyed scrap:	
Smelters, refiners, and ingot makers	379,000
Brass and wire-rod mills	448,000
Foundries, and miscellaneous manufacturers	38,600
Red brass:^a	
Smelters, refiners, and ingot makers	58,300
Brass mills	8,780
Foundries and miscellaneous manufacturers	10,100
Leaded yellow brass:	
Smelters, refiners, and ingot makers	28,800
Brass mills	404,000
Foundries and miscellaneous manufacturers	1,930
Yellow and low brass: all plants	53,900
Cartridge cases and brass: all plants	66,800
Auto radiators	
Smelters, refiners, and ingot makers	72,200
Foundries and miscellaneous manufacturers	4,470
Bronzes	
Smelters, refiners, and ingot makers	12,100
Brass mills and miscellaneous manufacturers	14,900
Nickel-copper alloys: all plants	17,800
Low-grade and residues	
Smelters, refiners, and miscellaneous manufacturers	87,100

Source: Edelstein 1998

^a Includes composition turnings, silicon bronze, railroad car boxes, cocks, and faucets, gilding metal, and commercial bronze.

Table C-11 (continued)

Scrap Type and Processor	Consumption (t)
Other alloy scrap^b	
Smelters, refiners, and ingot makers	38,400
Brass mills and miscellaneous manufacturers	6,570
Total alloyed scrap	
Smelters, refiners, and ingot makers	303,000
Brass mills	558,000
Foundries and miscellaneous manufacturers	24,100
Total Scrap	
Smelters, refiners, and ingot makers	682,000
Brass and wire-rod mills	1,010,000
Foundries and miscellaneous manufacturers	62,700

^b Includes refinery brass, beryllium copper, and aluminum bronze.

C.2.6 Aluminum Bronze Foundries

Aluminum bronzes may be produced from prealloyed ingots (see Section C.2.4) or from directly alloyed components. In the latter case, the copper is melted together with copper/iron and copper/nickel master alloys at 1,200°C under a charcoal cover (U.K. CDA 1999). The melt is then deoxidized with a copper/manganese alloy and the charcoal cover is removed. The manganese oxide is skimmed off at this point to prevent its subsequent reduction by aluminum. An aluminum/copper master alloy is next added in small increments. The melt is then degassed with nitrogen (which also facilitates mixing) and a small quantity of a fluoride-base flux is added to remove metal from the dross. The bronze is then cast into appropriate molds.

Melting of large charges in a reverberatory furnace may require use of a cover flux to reduce oxidation losses.

Melt temperature and melting time are kept to a minimum to control hydrogen pickup in the furnace. At 1,200°C, the hydrogen solubility in an aluminum bronze containing 8% Al is about 3.5 cm³/100 g and this increases to about 5.8 cm³/100 g at 1,400°C. (The solubility of hydrogen in pure copper at comparable temperatures is more than twice as high.)